

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia



FINAL REPORT

PROJECT NO. 215-173

A STUDY OF THE SYNTHESIS AND PROPERTIES OF
BICYCLO[2,2,2]-2,5,7-OCTATRIENE AND RELATED COMPOUNDS

By

JACK HINE

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DEPARTMENT OF ARMY PROJECT NO. 599-01-004

ORDNANCE R & D PROJECT NO. TB-0001

OCR PROJECT NO. 446 (Rev.)

OCR CONTRACT NO. DA-01-009-ORD-253

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JUNE 27, 1952, to JUNE 26, 1955

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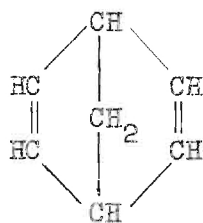
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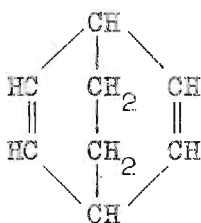
This Report Contains 25 Pages

I. ABSTRACT

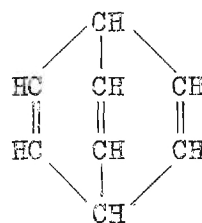
The object of this investigation was to prepare bicyclo[2,2,1]-2,5-heptadiene (I), bicyclo[2,2,2]-2,5-octadiene (II), and bicyclo[2,2,2]-2,5,7-octatriene (III) which has been named klovosene and to study their properties including particularly any interactions between the double bonds on adjacent bridges of their bicyclic ring systems.



I



II



III

Compound I has been prepared by the dehalogenation of 2,3-dichlorobicyclo[2,2,1]-5-heptene and by the dehydrohalogenation of 2-chlorobicyclo[2,2,1]-5-heptene. Since this work was started, however, it was learned that I was being studied extensively elsewhere so work on this compound was discontinued. Compound II was prepared by the dehydrohalogenation of a mixture of chloro-2-bromobicyclo[2,2,2]octanes.

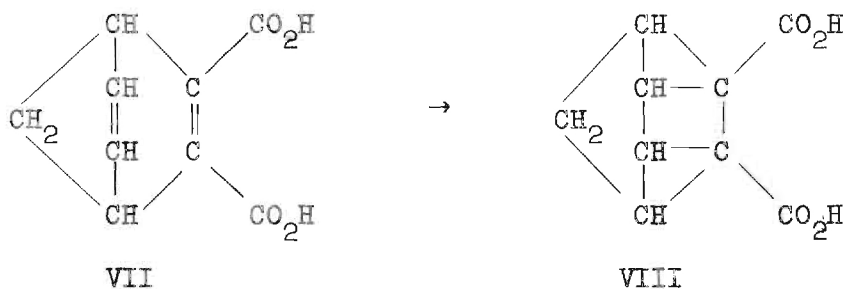
Attempts to prepare compound III were unsuccessful. Considerable attention was devoted to a study of the bromination of bicyclo[2,2,2]-2-octene by N-bromosuccinimide. The monobromination part of this reaction was found to yield largely rearranged products having the bicyclo[3,2,1]octane ring structure.

II. INTRODUCTION

Most of the work accomplished during the first two years of this project has been described in an article in the Journal of the American Chemical Society. A reprint of this article is included in the

appendix of this report. The introduction to this article describes the historical background and motivation for this work. However, since this article was first written, the results of several additional investigations in other laboratories where work in this field is being carried out have been learned. Several of the more relevant of these are described below.

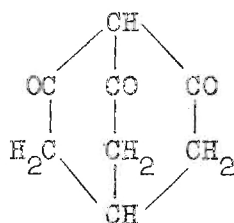
Julius Hyman and Company have reported the preparation of I in a patent.¹ Van Tamelen found no evidence for homoconjugation in a study of several of the addition reactions of 1,4-cyclohexadiene.² Cristol and Snell have reported that bicyclo[2,2,1]-2,5-heptadiene-2,3-dicarboxylic acid (VII³) upon irradiation with ultraviolet light isomerizes to tetracyclo[2,2,1,0^{2,6},0^{3,5}]heptane-2,3-dicarboxylic acid (VIII).⁴



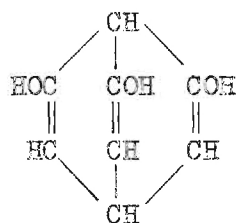
The existence of two different compounds corresponding to formulas VII and VIII rather than just one resonance stabilized compound for which VII and VIII are contributing structures adds considerably to the understanding of interactions between double bonds on adjacent bridges of bicyclic ring systems.

1. Julius Hyman and Co., Belgian Patent 498,176; Chem. Abs. 49, 372 (1955).
2. E. E. van Tamelen, J. Am. Chem. Soc. 77, 1704 (1955).
3. To avoid confusion the numbers IV, V and VI are omitted from the main body of this report since they refer to compounds described in the appendix.
4. S. J. Cristol and R. L. Snell, J. Am. Chem. Soc. 76, 5000 (1954).

The report, by Theilacker and Schmid, of the preparation of bicyclo[2,2,2]octane-2,6,7-trione (IX) is of great interest since this compound upon enolization could yield X, a trihydric phenol in the klovosene series.⁵



IX



X

While these workers did not report any search for the properties of X in their compound, it would appear that the existence of any major fraction of their material in the form of X would be too striking to overlook. The observations of Schwarzenbach and Wittwer on such simple monoketones as cyclohexanone and cyclopentanone⁶ show that the keto form is more stable than the enol by about 5 or 6 kcal per mole. The existence, then, of the bicyclooctatrione in form IX rather than X appears to show that the 15 to 18 kcal per mole that would be required for enolization are not repaid by any stabilization of the resultant molecule by interaction among the three double bonds. In other words, it appears that even if klovosene has some aromatic character, its resonance energy is less than 15 to 18 kcal per mole.

III. RESULTS AND DISCUSSION

After completing the synthesis of bicyclo[2,2,1]-2,5-heptadiene and bicyclo[2,2,2]-2,5-octadiene as described in the appendix, the

5. W. Theilacker and W. Schmid, Ann. 570, 15 (1950).

6. G. S. Schwarzenbach and C. Wittwer, Helv. Chim. Acta. 30, 656, 659, 663, 669 (1947).

project tried to synthesize klovosene (bicyclo[2,2,2]-2,5,7-octatriene) by analogous methods. The chlorination of 2-bromobicyclo[2,2,2]octane was carried out with an excess of sulfuryl chloride in an attempt to bring about dichlorination. Actually, an analysis showed that the product obtained contained between two and three chlorine atoms per molecule. When this material was subjected to the action of potassium anilide, the products included ethylene, acetylene, benzene, chlorobenzene, and bicyclo[2,2,2]-2,5-octadiene. However, no good evidence for the presence of klovosene was obtained. With potassium amide as a dehydrohalogenating agent, the same products were obtained except that phenylacetylene was present and benzene was absent.

It was then thought more desirable to prepare a larger amount of bicyclooctadiene in order to study the interactions between the double bonds of this compound. In an attempt to find a more convenient synthesis, the reaction of bicyclo[2,2,2]octene with N-bromosuccinimide (NBS) was studied. While this reagent is specific for brominating allylic positions, it does not seem likely that it would do so with bicyclooctene since the only allylic positions in this compound are at bridgeheads. Therefore, it was hoped to obtain 2-bromobicyclo[2,2,2]-5-octene. While a fraction A boiling at a narrow range corresponding to a monobromobicyclooctene was obtained in yields up to 22%, this fraction appeared to be a mixture of several compounds. Only 31% of it reacted with a refluxing solution of potassium t-butoxide after 6 hours. A study of the methanolysis showed that the extent of reaction approached 30% after more than a day at 40°. A plot of the extent of reaction versus time showed that the reactive 30% of A contained at least two and perhaps three components. Furthermore,

although crude A gave an immediate precipitate with ethanolic silver nitrate, material that had been refluxed with water for a while did not give this reaction, although analysis showed that plenty of halogen remained in the compound.

Fraction A was unsaturated and could be catalytically hydrogenated to a mixture B of saturated bromides. A comparison of the infrared spectrum of B with those of the only two possible monobromobicyclo[2,2,2]octanes, the 1- and 2- derivatives and of 2-bromobicyclo[3,2,1]octane showed that none of these compounds is a major constituent of B. Therefore, the nature of A and B was investigated more thoroughly.

Several bicyclooctane derivatives were prepared for use as reference compounds. The preparation of 2-bromobicyclo[3,2,1]octane by the silver bromide catalyzed rearrangement of 2-bromobicyclo[2,2,2]octane was carried out as described by Doering and Farber.⁷ While the product melted at the same temperature as that described by Farber, it was seen from its infrared spectrum to be contaminated with unrearranged 2-bromobicyclo[2,2,2]octane. Sodium in an isopropyl alcohol reduction of this mixture gave a solid mixture of saturated hydrocarbons. This mixture had all of the infrared absorption bands of pure bicyclo[2,2,2]octane and also a number of other bands which must be due to bicyclo[3,2,1]octane.

Bicyclo[2,2,2]-2-octene was hydrated with rearrangement to bicyclo[3,2,1]-2-octanol which was then transformed to 2-chlorobicyclo[3,2,1]octane, all by the method of Newman and Yu.⁸ The chloride was dehydrohalogenated with potassium anilide to bicyclo[3,2,1]-2-octene.

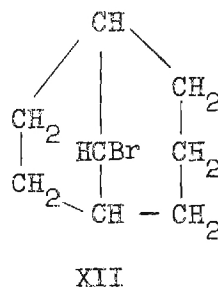
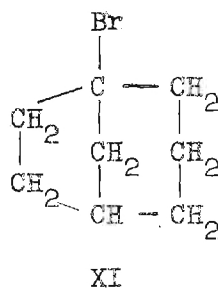
7. W. von E. Doering and M. Farber, J. Am. Chem. Soc. 71, 1514 (1949); M. Farber, Ph.D. Thesis, Columbia University, 1949.

8. M. S. Newman and Y. T. Yu, J. Am. Chem. Soc. 74, 507 (1952).

The major (unreactive) component of fraction A was shown to be a bicyclo[3,2,1]octane derivative by the following experiments. A solution of A in isoöctane was refluxed for several days with water containing suspended calcium hydroxide to remove the more reactive bromides. The remaining less reactive bromide was then reduced with sodium in alcohol to give a volatile unsaturated hydrocarbon shown by its spectrum to be bicyclo[3,2,1]-2-octene. When crude A was reduced with sodium in alcohol, the product also contained a little bicyclo[2,2,2]-2-octene showing that at least one of the reactive bromides had a bicyclo[2,2,2]octane ring skeleton. The catalytic hydrogenation of A yielded the solid mixture B. B was saturated and had the proper bromine analysis for a monobromobicycloöctane. Sodium in alcohol reduction gave bicyclo[3,2,1]octane containing a little bicyclo[2,2,2]octane.

It was attempted to locate the bromine atom in the bicyclo[3,2,1]octane ring system in the major constituents of A and B by the following method. Mixture B was refluxed with water for several days, but only the more active impurity appeared to react. The unreactivity of this major component of B and that of its unsaturated analog in A suggests the 1-bromo compound (XI) which should be unreactive due to the location of the halogen at a bridgehead,⁹ and the 8-bromo compound (XII), which might very well be unreactive since the carbonium ion should be destabilized by steric inhibition of hyperconjugation.¹⁰

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9. P. D. Bartlett and coworkers, J. Am. Chem. Soc. 61, 3184 (1939); 62, 1183 (1940); 72, 1005 (1950); W. von E. Doering and coworkers, ibid., 72, 1005 (1950); 75, 1008 (1953).
10. cf. J. D. Roberts, W. Bennett and R. Armstrong, J. Am. Chem. Soc. 72, 3329 (1950).



The 2-bromo compound has already been ruled out and the only other possibilities, the 3-bromo and 6-bromo compounds, offer no explanation for the unreactivity of the compound. Further evidence against the bromine's being in the 3- or 6- position was obtained by the reaction of B with potassium anilide. When this reaction was allowed to proceed for a short time, the product formed was largely a bromide shown by its infrared spectrum to be the unreactive bromide constituent of B. A small amount of bicycloöctenes was obtained but these probably arose from the reactive bromides. When the reaction was run for a longer time, the bromide reacted but apparently did not give dehydrohalogenation since the yield of bicycloöctenes was still very small and since a high molecular weight amine, presumably an N-bicycloöctyl-aniline, was obtained. No reason for such inertness toward dehydrohalogenation is apparent for the 3- or 6-bromo derivative, and, therefore, it seems more likely that the material is the 1- or 8-bromo compound, either of which may lose hydrogen bromide only to give a double bond at a bridgehead in violation of Bredt's rule. Of these two possibilities, the latter seems more likely since some of the unreactive bromide (recovered from the potassium anilide reaction) was oxidized to a ketone with silver chromate, a reaction that should not proceed with a tertiary halide like XI.

IV. EXPERIMENTAL

Chlorination of 2-Bromobicyclo[2,2,2]octane.--In a typical run, 450 g of 2-bromobicyclo[2,2,2]octane was refluxed for 7 hours with 880 ml of sulfuryl chloride in the presence of about 5 g of benzoyl peroxide. Distillation of the product gave 172 ml of material b.p. 137°-140°.

Anal. calculated for $C_8H_{11}BrCl_2$: 11.64 meq halogen per gram.
Calculated for $C_8H_{10}BrCl_3$: 13.64 meq halogen per gram. Found: 13.0 meq halogen per gram.

Dehydrohalogenation of Polychloro-2-Bromobicyclo[2,2,2]octane.--To about one liter of liquid ammonia in which 34 g of potassium had been dissolved in the presence of a piece of rusty iron, 52 g of polychloro-2-bromobicyclo[2,2,2]octane was added. After reaction appeared to be complete, the organic layer was taken up in ether and the ammonia was allowed to evaporate. The ether solution was then distilled through a fractionating column attached to a gas-collection apparatus. A gas, shown by its infrared spectrum to be a mixture of ethylene and acetylene, was collected. Continuation of the distillation yielded, between 69° and 80° at 95 mm, a mixture whose infrared spectrum showed it contained chlorobenzene, phenylacetylene, and bicyclo[2,2,2]-2,5-octadiene.

The potassium anilide dehydrohalogenations were carried out in a manner similar to the other potassium anilide reactions described in this report. The reaction products were ethylene, acetylene, chlorobenzene, benzene, and bicyclo[2,2,2]-2,5-octadiene.

The Reaction of Bicyclo[2,2,2]-2-octene with NBS.--A solution of 112 g (1.04 moles) of bicyclooctene in 385 ml of carbon tetrachloride was refluxed with 200 g (1.12 moles) of N-bromosuccinimide and a catalytic quantity of benzoyl peroxide for 2 hours. The solution was then filtered

to remove succinimide and unreacted NBS and fractionated, first at atmospheric pressure and later at 50-100 mm, to remove the carbon tetrachloride and unreacted bicyclooctene. The fractionation was continued at 28 mm with 5 ml of product being collected at 84°-98°, 27 ml at 98°-101°, and 2 ml at 101°-110°. The 27-ml fraction was called A and found to weigh 37.9 g (d_4^{26} 1.405). If the material is a monobromobicyclooctene as other evidence indicates, the yield in this run was 0.203 mole or 20%. The corresponding fractions from other runs were found to have essentially identical infrared spectra.

Anal. calculated for $C_8H_{11}Br$: Br, 42.71. Found: Br, 43.7.

The presence of an infrared band at 6.07 μ suggested and the decoloration of bromine in carbon tetrachloride confirmed the unsaturated character of A. Infrared spectra also showed that A contained no significant amount of 2-bromobicyclo[2,2,2]-2-octene.

2,3-Dibromobicyclo[2,2,2]octane.--To a solution of 108 g (1.0 mole) of bicyclo[2,2,2]-2-octene in 20 ml of carbon tetrachloride and 2 ml of acetic acid was added 173 g (1.08 moles) of bromine. The product was fractionated at 20 mm, and the fractions collected between 135° and 144° were found to weigh 110 g. These fractions were part solid and part liquid. After repeated recrystallizations from pentane (cooling in a dry-ice bath), about one fourth of this material could be obtained as white crystals m.p. 53.5°-55.0°.

Anal. calculated for $C_8H_{12}Br_2$: C, 35.85; H, 4.51; Br, 59.64.
Found: C, 36.04; H, 4.48; Br, 59.41.

Evidence for the structure assigned to this dibromide was obtained by allowing 1.6 g to react with an excess of metallic potassium in an isopropyl alcohol solution. When reaction was complete, the solution

was distilled and water was added to the distillate, precipitating a white solid whose infrared spectrum showed it to be bicyclo[2,2,2]-2-octene.

2-Bromobicyclo[2,2,2]-2-octene.--A solution of 13.3 g (46 m moles) of 2,3-dibromobicyclo[2,2,2]octane in 50 ml of 1.29 N potassium t-butoxide in t-butyl alcohol was allowed to reflux for 1 hour. Most of the t-butyl alcohol was removed by distillation, and water was added to the residue. The organic layer that separated was taken up in pentane, dried, and distilled in vacuum to yield 8.5 g of a water white liquid, b.p. 90°-110°, at 35 mm. This material was fractionated at 40 mm to yield 7.25 g (84%) of material, b.p. 100°-101°, n_D^{23} 1.5315.

Anal. calculated for $C_8H_{11}Br$: C, 51.35; H, 5.92; Br, 42.71. Found: C, 51.68; H, 6.17; Br, 41.91.

The Reaction of Fraction A with Potassium t-Butoxide in t-Butyl Alcohol.--

To a refluxing solution of 8 g (0.2 mole) of potassium in t-butyl alcohol was added 30 g (0.17 mole) of fraction A. A white precipitate was formed almost immediately but refluxing was continued for 6 hours.

The precipitated potassium bromide was collected on a filter, dissolved in water, and titrated with standard silver nitrate solution. The amount of halide ion corresponded to 31% reaction. From the filtered t-butyl alcohol solution, only unreacted organic bromides could be obtained.

The Methanolysis of Fraction A.--A dilute solution of A in methanol

was allowed to solvolyze at 40°. At intervals, samples were pipetted into methanol at 0° and titrated with standard sodium methoxide to the rosolic acid end point. The following results were obtained:

<u>Time</u> (min)	<u>Reaction</u> (%)	<u>Time</u> (min)	<u>Reaction</u> (%)
2.33	9.5	215	19.5
25.9	13.6	1130	23.1
37.3	14.3	1540	28.4
59.5	16.1		

Between the last two points, the thermoregulator failed and the temperature rose above 40°. From a comparison of the first point with any subsequent point, it seems obvious that at least two compounds are hydrolyzing. Inspection of a logarithmic plot suggests that there may be three.

Catalytic Hydrogenation of A to give B.--Seven grams of A was dissolved in 10 ml of absolute ethanol, a little platinum oxide was added, and the solution was shaken under 50 psi of hydrogen for 2 hours. The solid product weighed 5.5 g, melted at 75°-78° after one recrystallization from hexane, and was called mixture B. It did not decolorize bromine in carbon tetrachloride, but it did give a precipitate with ethanolic silver nitrate. After nine recrystallizations from pentane, B melted at 87°-87.5° and gave no reaction with silver nitrate. A comparison of infrared spectra showed that B (either that melting at 75°-78° or that at 87°-87.5°) contained neither 1-bromo-¹¹ nor 2-bromo-bicyclo[2,2,2]octane nor 2-bromobicyclo[3,2,1]octane as a major constituent.

2-Bromobicyclo[3,2,1]octane.--Following the directions of Doering and Farber⁷, 4 g of 2-bromobicyclo[2,2,2]octane was refluxed with 4 g of freshly prepared and dried silver bromide in carbon tetrachloride for 2 hours. Filtration and fractionation gave a product boiling at 107°-108° (29 mm), m.p. 44°-46°. Farber's product melted at 41°-43°. While

11. A. A. Sayigh, Ph. D. Thesis, Columbia University, 1952.

the infrared spectrum of this material contained all the bands characteristic of 2-bromobicyclo[2,2,2]octane, it also contained other bands which were attributed to 2-bromobicyclo[3,2,1]octane.

A solution of 1.57 g of the product was refluxed for 5 hours with 5 g of sodium in isopropyl alcohol, and the alcohol was then distilled. Addition of water to the distillate gave 0.4 g of a white solid that melted at 150°-152° after recrystallizations from nitromethane. This material had all of the infrared bands characteristic of bicyclo[2,2,2]octane and additional ones that were attributed to bicyclo[3,2,1]octane.

Reaction of A with Sodium in Isopropyl Alcohol.--In a typical run, 5 ml of A in 15 ml of isooctane was refluxed for 8 days with 50 ml of water and 1.8 g of calcium oxide. Fractionation of the isooctane layer gave 2 ml of product, b.p. 103°-107° at 31 mm. The sample of A from which the reactive bromides had thus been removed gave no precipitate with boiling ethanolic silver nitrate but did contain halogen as shown by reaction with sodium. A solution of 1.5 g of the material whose preparation is described above in 50 ml of isopropyl alcohol was refluxed with 5.4 g of sodium. Water was added to the distillate from this reaction mixture to give an organic layer that yielded about 1 ml of a liquid product. This volatile liquid decolorized bromine and from its infrared spectrum appears to be bicyclo[3,2,1]-2-octene by comparison with material prepared by the method of Newman and Yu.⁸

When crude A was used in this reaction, the unsaturated hydrocarbon product obtained was solid and its spectrum showed that bicyclo[2,2,2]-2-octene was present.

Reaction of B with Sodium in Isopropyl Alcohol.--When B was reduced with sodium in isopropyl alcohol in the manner described for other bromides, the product in one run melted at 138° and in another run at 149°-150°. Both products were saturated and had infrared spectra very much like that of the mixture of bicyclo[3,2,1]octane and bicyclo[2,2,2]octane prepared by the reduction of the impure 2-bromobicyclo[3,2,1]octane.

Attempted Hydrolysis of B.--When B was subjected to hydrolysis conditions of the type described for A, unreacted B could be recovered although its infrared spectrum showed that some constituents had been removed. Separate experiments showed that the reaction conditions employed were sufficient to bring about the hydrolysis of 2-bromobicyclo[2,2,2]octane and 2-bromobicyclo[3,2,1]octane in good yield.

Reaction of B with Potassium Anilide.--A solution of 5 g of B in 5 ml of aniline was added to 50 ml of aniline in which 3.5 g of potassium had been dissolved. The acid insoluble part of the distillate contained B along with bicycloöctenes. When some of the solution that had stood overnight was distilled, unreacted B was also obtained. However, when the aniline solution was refluxed for 1 hour and 15 minutes before distillation, the product contained somewhat less B. The residue from this latter reaction after steam distillation, acid extraction, and basic precipitation gave a compound that appeared to be a high molecular weight amine.

Silver Chromate Oxidation of B.--When 0.5 g of the B that had been recovered from the reaction with potassium anilide had refluxed for 160 hours with 1.1 g of silver chromate in acetonitrile, the resulting solution was filtered and added to aqueous ethanol. The resultant

solution upon treatment with 2,4-dinitrophenylhydrazine gave a small amount of crystals. This result was not obtained in a blank run in the absence of bromide.

V. CONCLUSIONS AND RECOMMENDATIONS

Although it has been shown that bicyclo[2,2,2]-2,5-octadiene may be synthesized, the interaction between the two double bonds on adjacent bridges in the bicyclic ring system of this compound has not been studied. Such a study should be of interest since interaction has been reported for bicyclo[2,2,1]-2,5-heptadiene. While attempts to prepare klovosene (III) were not successful, they were certainly not complete enough to suggest that the compound should be incapable of existence. It would be desirable to carry out further work on the monobromination products from the reaction of bicyclo[2,2,2]-2-octane with N-bromosuccinimide in order to draw more definite conclusions about their structure.

VI. PERSONNEL AND ACKNOWLEDGMENTS

The work described in this report was carried out by John A. Brown, Graduate Assistant, from July 1952 until June 1954, Leon H. Zalkow, Graduate Assistant, from June 1952 until June 1955, and Jack Hine, the Project Director.

We wish to acknowledge help on many phases of this work from William E. Gardner and Mildred Hine, who were simultaneously engaged in related research problems in the Georgia Tech School of Chemistry.

Approved:

Respectfully submitted:

Paul K. Calaway, Director
Engineering Experiment Station

Jack Hine
Project Director

VI. APPENDIX

[Reprinted from the Journal of the American Chemical Society, **77**, 594 (1955).]
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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

The Synthesis of Bicyclo[2,2,2]-2,5-octadiene^{1,2}

By JACK HINE, JOHN A. BROWN, LEON H. ZALKOW, WILLIAM E. GARDNER AND MILDRED HINE

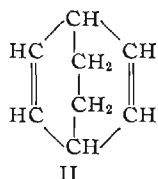
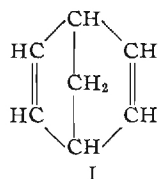
RECEIVED JULY 15, 1954

A synthesis is reported for bicyclo[2,2,2]-2,5-octadiene (II), a compound of particular interest because of unusual possibilities for interaction between non-conjugated double bonds. Two syntheses, one involving the dehalogenation of 2,3-dichlorobicyclo[2,2,1]-5-heptene and the other the dehydrohalogenation of 2-chlorobicyclo[2,2,1]-5-heptene, are reported also for the related compound bicyclo[2,2,1]-2,5-heptadiene (I). The preparation of II was accomplished by the dehydrohalogenation of a mixture of monochloro-2-bromobicyclo[2,2,2]octanes. The structures of I and II are proven by their reduction (by two moles of hydrogen) to the corresponding saturated hydrocarbons. In addition, II has been shown to form a crystalline tetrabromide and to yield ethylene and benzene upon pyrolysis. An improved method of preparing 1,3-cyclohexadiene also is reported.

Introduction

There have been recently reported several studies of what we shall call *homoconjugation*, in which an olefinic double bond interacts with an atom which is separated from the nearest unsaturated carbon by one saturated carbon atom. These studies include the *i*-cholesteryl rearrangement,³ rearrangements of dehydronorbornyl compounds to nortricycylene derivatives,⁴ the acetolysis of 3-phenyl-2-butyl *p*-toluenesulfonate⁵ and related reactions,⁶ etc.

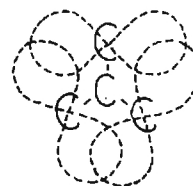
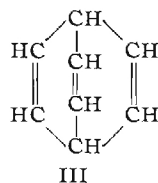
We were interested therefore in learning whether the effects of homoconjugation could be detected in the reactions of bicyclo[2,2,1]-2,5-heptadiene (I) and bicyclo[2,2,2]-2,5-octadiene (II).



Such homoconjugation might reasonably be expected since the double bonds are so situated that their π -orbitals should overlap somewhat.⁷

We were further interested in learning whether this sort of interaction between double bonds on adjacent bridges of a bicyclic ring system might give aromatic character to bicyclo[2,2,2]-2,5,7-octatriene (III). A view of III from the top suggests that the π -orbitals of the double bonds might overlap enough for the formation of a somewhat cylin-

drical molecular orbital (containing six electrons) around the middle of the molecule.⁷



Top view of III

However, it may also be seen to be impossible to arrange the π -orbitals in a way which gives all overlapping lobes the same algebraic sign, as is said to be required.⁷ Because this is the first case known to us in which the *sign* of an atomic orbital has been of such importance, compound III is of particular interest. While some derivatives of I and II such as the 2- and 3-carboxy compounds are known,⁸ any study of interaction between the carbon-carbon double bond in these derivatives would be greatly complicated by the interaction of one of the double bonds with the functional group(s). Triptycene⁹ can be thought of as the tribenzo derivative of III but the π -electrons in this compound may be too occupied with the benzenoid resonance to permit much interaction between adjacent bridges, although the difference in absorption spectra between triptycene and triphenylmethane has been attributed to such interaction.^{9b}

Since this investigation was begun, Parham, Hunter, Hanson and Lahr have reported the preparation of a small amount of material which was probably the bicycloheptadiene, I.¹⁰ This compound was prepared by the Chugaev degrada-

- (1) Sponsored by the Office of Ordnance Research, U. S. Army.
- (2) Taken in part from the Ph.D. thesis of John A. Brown, 1954.
- (3) C. W. Shoppee, *J. Chem. Soc.*, 1147 (1946); S. Winstein and R. Adams, *THIS JOURNAL*, **70**, 838 (1948); R. G. Pearson, L. A. Subluskey and L. C. King, *ibid.*, **70**, 3479 (1948).
- (4) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).
- (5) D. J. Cram, *ibid.*, **71**, 3863 (1949).
- (6) Cf. E. M. Kosower, *Science*, **113**, 605 (1951).
- (7) For a discussion of π -orbitals and their interactions to form multiple bonds and aromatic rings see C. A. Coulson, "Valence," Oxford University Press, London, 1952, Sections 4.7, 8.7 and 9.1.

- (8) K. Alder, G. Stein, S. Schneider, M. Liebmann, E. Roiland and G. Schulze, *Ann.*, **525**, 183 (1936); O. Diels, K. Alder and H. Nienburg, *ibid.*, **490**, 236 (1931); K. Alder and H. F. Rickert, *Ber.*, **70B**, 1364 (1937).
- (9) (a) P. D. Bartlett, M. J. Ryan and S. G. Cohen, *THIS JOURNAL*, **64**, 2649 (1942); (b) P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950).
- (10) W. E. Parham, W. T. Hunter, R. Hanson and T. Lahr, *ibid.*, **74**, 5646 (1952).

tion of dehydronorborneol and it reacted with phenyl azide to give a product having the composition of one mole of I plus two of phenyl azide. These workers point out that I is not formed easily, attempted preparations by the acetate pyrolysis method and the Hofmann degradation of the quaternary ammonium hydroxide being unsuccessful.

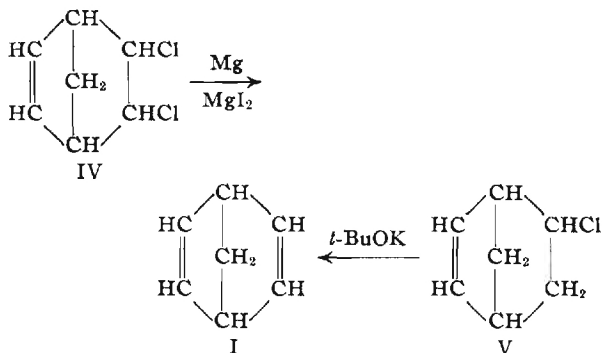
The use of I as an intermediate in preparing the insecticide Aldrin is reported in a patent by Lidov.¹¹ In this patent the preparation of I is not described but is said to be the subject of a pending patent application.¹²

We have learned also that the interaction between the double bonds of I has been studied in some detail by Dr. Saul Winstein who has found evidence for homoconjugation in several cases.¹³ We have therefore given I no attention in this regard and plan to study only II and III. We did, however, continue studying methods for synthesizing I for use as "model" reactions for the synthesis of II and III because the commercial availability of dicyclopentadiene makes most bicyclo[2,2,1]heptane derivatives more readily obtainable than the corresponding bicyclo[2,2,2]octane compounds.

Results and Discussion

The attempted dehydration of dehydronorborneol being unsuccessful, we next tried to dehalogenate 2,3-dichlorobicyclo[2,2,1]-5-heptene (IV). Sodium iodide in acetone gave no reaction, but dechlorination was accomplished by use of a mixture of magnesium and magnesium iodide in *n*-butyl ether.

The bicycloheptadiene was prepared also by the dehydrohalogenation of 2-chlorobicyclo[2,2,1]-5-heptene (V). Quinoline was not useful for this purpose, but with potassium *t*-butoxide a 25% yield was obtained.



The hydrocarbon thus prepared was a colorless, mobile liquid boiling at 89.5°. Its structure is established by its methods of synthesis, its elemental analysis and its catalytic hydrogenation (requiring two moles of hydrogen) to bicyclo[2,2,1]-heptane.

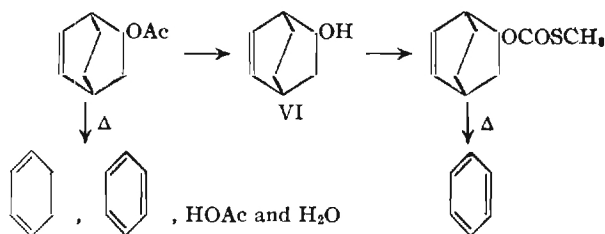
Since most of the useful methods of entry into the bicyclo[2,2,2]octane series involve the Diels-Alder addition of various unsaturated compounds to 1,3-cyclohexadiene, we were interested in finding

a convenient method for preparing this compound in fairly large quantities on a laboratory scale. We have found that the dehydrohalogenation of cyclohexene dibromide by quinoline¹⁴ yields more cyclohexene and benzene than cyclohexadiene.¹⁵ On the other hand, while the method of Hofmann and Damm, in which most of the diene is obtained by the potassium bisulfate catalyzed de-ethanolation of 3-ethoxycyclohexene,¹⁶ gives a much purer product, the preparation requires an extra step and involves a somewhat tedious separation of ethanol from the product.

We have found that triethanolamine or tri-*n*-butylamine gives no better a product than does quinoline, but that with sodium hydroxide in ethylene glycol solution, cyclohexene dibromide may be transformed rapidly and in good yield to 1,3-cyclohexadiene of about 80% purity. Since the benzene and cyclohexene present as impurities do not interfere with the subsequent Diels-Alder reactions this material is satisfactory for our purposes.

The synthesis of the bicyclooctadiene II was first attempted by methods analogous to those which were successful in the preparation of I. The addition of *trans*-1,2-dichloroethylene to cyclohexadiene gave a poor yield of a product boiling over a fairly narrow range at about the expected temperature for 2,3-dichlorobicyclo[2,2,2]-5-octene. Its chemical analysis and certain other properties, however, suggested that the desired product was mixed with a somewhat larger quantity of dicyclohexadiene. No product was isolated when this impure product was treated with magnesium-magnesium iodide.

We also attempted to prepare II from the alcohol VI by the acetate pyrolysis and Chugaev methods. Only benzene, cyclohexadiene, acetic acid and water were identified as products of the acetate pyrolysis, while only benzene was isolated in the Chugaev reaction.



The oxidative bisdecarboxylation reaction of Doering, Farber and Sayigh¹⁷ on bicyclo[2,2,2]-5-octene-2,3-dicarboxylic anhydride also gave us none of compound II. We next tried a dehydrohalogenation method. Bicyclo[2,2,2]-2-octene was prepared by the Diels-Alder addition of ethylene to cyclohexadiene, and to the octene was added hydrogen bromide.¹⁸ The resultant 2-bromobicyclo[2,2,2]-octane was chlorinated with sulfuryl chloride. The mixture of monochlorides, separated from polychlorides by fractionation, should contain a consid-

(14) A. W. Crossley, *J. Chem. Soc.*, **85**, 1403 (1904).

(15) Cf. K. W. F. Kohrausch and R. Seka, *Ber.*, **68B**, 528 (1935).

(16) F. Hofmann and P. Damm, *Chem. Zentr.*, **97**, I, 2342 (1926); *C.A.*, **21**, 1249 (1928).

(17) W. von E. Doering, M. Farber and A. Sayigh, *This Journal*, **74**, 4870 (1952).

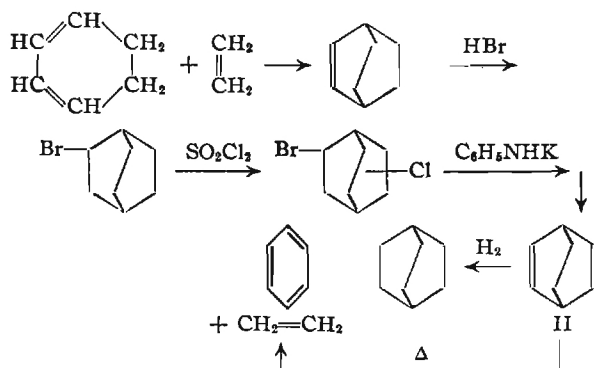
(18) W. von E. Doering and M. Farber, *ibid.*, **71**, 1514 (1949).

(11) R. E. Lidov, U. S. Patent 2,635,977 (April 21, 1953) assigned to Shell Development Company.

(12) Hyman, Freireich and Lidov, Patent Application, U. S. Serial No. 45,574.

(13) S. Winstein, private communication.

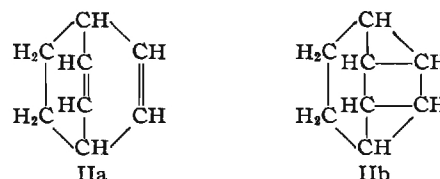
erable percentage of the 5- and 6-chloro compounds, the only isomers capable of dehydrohalogenation to II, due to the tendency in free radical chlorination to avoid substitution on the same carbon as, or one adjacent to, a halogen atom already present.¹⁹ We were unable to isolate any II from the action of potassium *t*-amylate on the mixture of monochloro-2-bromobicyclo[2,2,2]-octanes, but reaction with potassium anilide gave a small yield of II and also benzene and ethylene.



The structural formula assigned II is in agreement with its elemental analysis, physical properties and method of synthesis, but further evidence was obtained as follows. The catalytic hydrogenation of II required two moles of hydrogen and produced bicyclo[2,2,2]octane. The addition of bromine gave a crystalline tetrabromide. The infrared spectrum of II (Fig. 1) shows maxima at 6.13

and 6.29 μ , in the characteristic region for carbon-carbon double bonds. Upon pyrolysis, II underwent a reverse Diels-Alder reaction to yield benzene and ethylene. The fact that this pyrolysis does not occur at a reasonable rate when II is distilled or even heated with potassium anilide in aniline or in decalin, but requires a dull red glowing wire, suggests that the benzene and ethylene by-products in the preparation of II do not arise from its decomposition.

These data, however, do not distinguish unequivocally between the structural formulas IIa and IIb or even make clear whether IIa and IIb are



structures for two different compounds or merely two different resonance structures contributing to the total structure of one compound.²⁰ The problem thus stated in terms of valence bond resonance is essentially the one we already described in terms of atomic and molecular orbitals in the introduction. We hope to work toward its answer, the nature of the interaction between double bonds on adjacent rings of a bicyclic ring system, by further studies on II and by attempting to prepare and study III.²¹

Experimental²²

Attempted Dehydration of Dehydro- α -norborneol.—Dehydro- α -norborneol prepared from its acetate by the method of Alder and Rickert²³ was heated with phosphorus pentoxide in xylene solution. Distillation of the reaction mixture gave no product more volatile than xylene.

Attempted Dehalogenation of 2,3-Dichlorobicyclo[2,2,1]-5-heptene.—A solution of 2,3-dichlorobicyclo[2,2,1]-5-heptene²⁴ and sodium iodide in acetone was refluxed for three hours and allowed to stand for several days. No precipitate of sodium chloride or iodine color was formed.

Bicyclo[2,2,1]-2,5-heptadiene (I). A. From 2,3-Dichlorobicyclo[2,2,1]-5-heptene.—The dehalogenation reagent was prepared in a manner similar to that described by Summerbell and Umhoefer²⁴ by adding 198 g. (0.78 mole) of iodine to 48.6 g. (2.0 moles) of magnesium in 630 ml. of di-*n*-butyl ether. To this refluxing solution was added 132 g. (0.81 mole) of 2,3-dichlorobicyclo[2,2,1]-5-heptene²⁴ dropwise with stirring. The contents of the flask were then distilled to dryness and the distillate fractionally redistilled. Between 86 and 89° (atm.) 19 g. (25% yield) of product was obtained, which upon refractionation gave 14.4 g., b.p. 89–89.5° (atm.), n_D^{20} 1.4670, d_4^{20} 0.8992. According to Lidov, bicyclo[2,2,1]-2,5-heptadiene boils in the range 85–90° at 630 mm.¹¹

Anal. Calcd. for C_7H_8 : C, 91.25; H, 8.75. Found: C, 91.20; H, 8.95.

B. From 2-Chlorobicyclo[2,2,1]-5-heptene.—Thirty grams (0.233 mole) of 2-chlorobicyclo[2,2,1]-5-heptene²³ was added to 300 ml. of *t*-butyl alcohol in which 19.5 g. (0.5

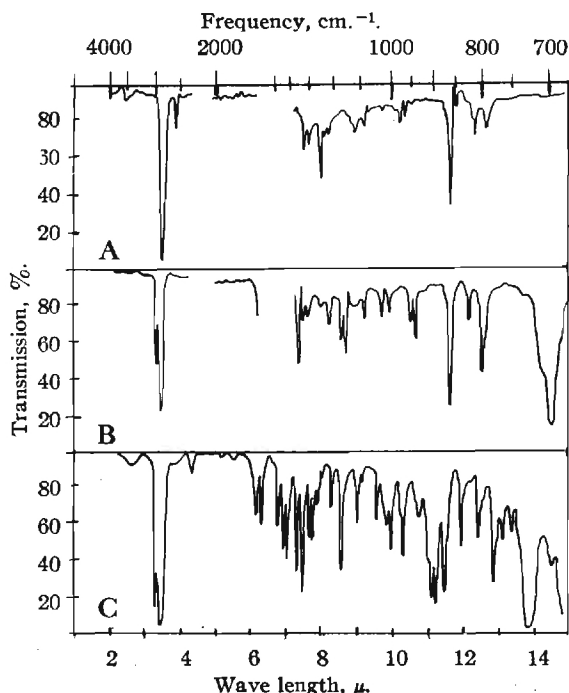


Fig. 1.—Infrared spectra of: A, bicyclo[2,2,2]octane in carbon disulfide; B, bicyclo[2,2,2]-2-octene in carbon disulfide; C, bicyclo[2,2,2]-2,5-octadiene.

(19) D. V. Tishchenko, *J. Gen. Chem. (U.S.S.R.)*, **7**, 658 (1937); *C. A.*, **31**, 5755¹ (1937); M. S. Kharasch and H. C. Brown, *THIS JOURNAL*, **61**, 2142 (1939); A. L. Henne and J. B. Hinkamp, *ibid.*, **67**, 1197 (1945).

(20) ADDED IN PROOF.—S. J. Cristol and R. L. Snell (*ibid.*, **76**, 5000 (1954)) have reported the existence of two distinct compounds of the type of IIa and IIb for the 2,3-dicarboxylic acid derivative of I.

(21) We should like to suggest for III the name *klovosene* (from the Greek *κλωβός*, bird-cage) which we have been using informally for the compound for several years.

(22) Melting points and boiling points uncorrected. Analyses by Clark Microanalytical Laboratory, Urbana, Ill.

(23) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1940).

(24) R. K. Summerbell and R. R. Umhoefer, *THIS JOURNAL*, **61**, 3016, 3020 (1939).

mole) of potassium had been dissolved. Since no potassium chloride had been precipitated after the solution was refluxed for an hour and then allowed to stand for a week, the material was slowly distilled through a fractionating column. The first distillate was essentially pure *t*-butyl alcohol, but as the pot temperature rose a reaction appeared to take place and the odor of the bicycloheptadiene became apparent. The last 40 ml. of distillate was therefore diluted with a large excess of water and an oily layer separated. This oil was dried over calcium chloride, mixed with some *o*-xylene (to serve as a distillation base) and fractionally distilled. The fraction boiling at 89.5–90° weighed 5.4 g. (25% yield) and its infrared spectrum was identical to that of the material whose preparation is described above.

Compound I was found to require 1.97 ± 0.1 moles of hydrogen for reduction by Adams catalyst in ethanol to material identical in boiling point, odor and infrared spectrum to bicyclo[2,2,1]heptane prepared by the method of Roberts, Urbanek and Armstrong.²⁵

1,3-Cyclohexadiene.—All of our preparations of cyclohexadiene utilized cyclohexene dibromide as the starting material. This material was prepared by adding bromine directly to cyclohexene containing a small amount of ethanol or acetic acid and kept below 0°. By use of a Dry Ice cooling bath the addition could be carried out relatively rapidly.

Two hundred seventy-five grams (1.7 moles) of cyclohexene dibromide was added to 875 g. (4.73 moles) of tri-*n*-butylamine at 200°. The crude product was distilled continuously from the reaction mixture and when fractionated gave 95 g. (70% yield, if pure diene) of material boiling at 80°. The refractive index showed that this material probably contained at least 50% cyclohexene. The use of quinoline¹⁶ gave results similar to this and a smaller yield of even less pure product was obtained with triethanolamine.

Sodium hydroxide in ethylene glycol solution (we were actually dealing with the sodium salt of ethylene glycol, no doubt) proved to be the most suitable dehydrohalogenating agent for our use. The method described below is the result of a considerable, but by no means complete, search for the optimum operating conditions. Four liters of ethylene glycol was placed in a 12-l. three-necked flask equipped with a vapor-tight stirrer, a thermometer whose bulb was in the liquid, a dropping funnel, and a 36-in. fractionating column, 1 in. in diameter and packed with glass helices. Two kilograms (50 moles) of sodium hydroxide was added and the flask was heated and its contents stirred until they reached 230°, when about 700 ml. of water had been distilled from the solution. Stirring is needed to prevent the dangerously sudden and exothermic solution of the alkali at about 140° and to break up the foam produced above 200°. At temperatures much above 230° the evolution of hydrogen gas from the reaction mixture becomes a major competing reaction. At this point 4 kg. (16.5 moles) of cyclohexene dibromide was added over a period of three hours, while a mixture of crude product and water distilled from the reaction mixture. The temperature in the reaction flask was kept between 220 and 230° and that in the head of the distilling column below 100°. The 1300 g. of organic layer in the distillate was separated from a similar amount of water, dried over calcium chloride and fractionally distilled. Between 79 and 82°, 980 g. was collected. From the refractive index (n_D^{20} 1.4689) and infrared spectrum it was estimated that the material was 81% cyclohexadiene, 15% cyclohexene and 4% benzene. The yield of cyclohexadiene was therefore 60%.

The use of sodium hydroxide in triethanolamine solution gave no better results, and furthermore this method has the disadvantage of requiring a larger amount of a more expensive solvent to dissolve a given amount of sodium hydroxide. Diethylene glycol may be substituted for ethylene glycol as the reaction solvent, provided at least 3 ml. of glycol per gram of sodium hydroxide is used. If a smaller ratio of diethylene glycol to alkali is used a dangerously exothermic reaction between the two takes place at temperatures somewhat above 200°.

Attempted Preparation and Dehalogenation of 2,3-Dichlorobicyclo[2,2,2]-5-octene.—Sixteen grams of 50% 1,3-cyclohexadiene (0.1 mole) and 9.7 g. (0.1 mole) of *trans*-dichloroethylene were heated in a sealed glass tube to 180–

220° for 22 hours. Distillation of this reaction mixture yielded 3.5 g. of material boiling at 90–93° (10 mm.). From the boiling point, method of preparation and analysis, the mixture appeared to contain 2,3-dichlorobicyclo[2,2,2]-5-octene and a somewhat larger amount of cyclohexadiene dimer.^{16,26} Variations in the reaction temperature, time and ratio of reactants gave no significant improvement in this method.

Attempted dehalogenation of 30 g. of the impure material prepared as described above by use of 12 g. of magnesium and 40 g. of iodine in a procedure like that described for I gave no significant quantity of material more volatile than the di-*n*-butyl ether solvent.

2-Acetoxybicyclo[2,2,2]-5-octene and its Pyrolysis.—This compound was prepared by a method like that of Alder and Rickert²³ who give few experimental details and none of the physical properties of the product, however. A small amount of hydroquinone, 175 g. of 81% 1,3-cyclohexadiene (1.77 moles) and 190 g. (2.21 moles) of vinyl acetate was kept around 180° for five days in a high pressure reaction vessel. Fractional distillation yielded 109 g. (37% yield) of product, b.p. 125–130° (44 mm.), n_D^{20} 1.5020. Decomposition of this acetate did not occur at a reasonable rate at its boiling point, 217° (atm.), and so it was distilled through a tube packed with glass helices and wrapped with wire heated to a dull red color. The product was a bright yellow liquid which upon fractional distillation gave appreciable amounts only of a wet mixture of benzene and cyclohexadiene, b.p. 75–77° (identified by infrared spectra) and of acetic acid, b.p. 110–113° as products boiling below 180°.

Chugaev Degradation of Bicyclo[2,2,2]-5-octen-2-ol.—Thirty-six grams (0.29 mole) of bicyclo[2,2,2]-5-octen-2-ol²⁷ and 11.4 g. (0.29 mole) of potassium were heated in 400 ml. of freshly distilled decalin. When all of the potassium had reacted 200 ml. of ether and 40 g. of carbon disulfide were added, and after two hours of stirring at reflux 90 g. of methyl iodide was added. The ether and excess carbon disulfide and methyl iodide were removed by fractionation and the xanthate was pyrolyzed by distilling the residue to dryness. The distillate was washed with aqueous alkali and mercuric chloride to remove carbonyl sulfide and mercaptans, then dried and fractionally distilled. Fraction 1, 2.5 ml., b.p. 44–77°, appeared to be only wet benzene and fraction 2, 5.5 ml., b.p. 77–78°, essentially pure benzene from their infrared spectra. No other fraction was found below the boiling point of decalin.

Attempted Bisdecarboxylation of Bicyclo[2,2,2]-5-octene-2,3-dicarboxylic Anhydride.—Following the general procedure of Doering, Farber and Sayigh,¹⁷ 6.9 g. (0.038 mole) of bicyclo[2,2,2]-5-octene-2,3-dicarboxylic anhydride²⁸ in 75 ml. of decalin was heated to reflux with 30 g. of lead dioxide. When the evolution of carbon dioxide had stopped the liquid was decanted, the solid washed with decalin and then added to the decanted liquid. Distillation of the decalin solution yielded no material boiling below 185°.

Bicyclo[2,2,2]-2-octene.—A 1500-ml. capacity Aminco high pressure reaction vessel containing 450 ml. of cyclohexadiene prepared as described (3.75 moles of pure diene) was charged with ethylene to a pressure of 750 p.s.i.²⁹ The reaction vessel was kept at $280 \pm 30^\circ$ for 34 hours and then cooled and opened. Distillation of the contents yielded 95 ml. of material boiling below 130° (largely at 80–85°) and 218 g. (54% yield) of material, b.p. 130–135° (largely 134°), m.p. 110–113°. Seka and Trampusch state that bicyclo[2,2,2]-2-octene melts at 113–114°³⁰ and although Doering, Farber and Sayigh list a m.p. of 141–144° they may have intended to write 111–114° since they quoted Seka and Trampusch's m.p. as 143–144°.¹⁷

Monochloro-2-bromobicyclo[2,2,2]octane.—Seventy-five grams (0.4 mole) of 2-bromobicyclo[2,2,2]octane, prepared by the addition of hydrogen bromide to bicyclo[2,2,2]-2-octene,¹⁸ 102 g. (0.75 mole) of sulfuric chloride and a small

(26) K. Alder and G. Stein, *Ann.*, **496**, 197 (1932).

(27) W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, **19**, 381 (1954).

(28) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

(29) The analogous Diels-Alder addition of cyclohexadiene to propylene has been described by G. Calingaert, H. Soroos and H. Shapiro, *Ind. Eng. Chem.*, **36**, 1055 (1944). ADDED IN PROOF.—H. M. Walborsky and D. F. Loncrini (THIS JOURNAL, **76**, 5396 (1954)) have reported this method of preparing the bicyclooctene.

(30) R. Seka and O. Trampusch, *Ber.*, **75B**, 1379 (1942).

(25) J. D. Roberts, L. Urbanek and R. Armstrong, *THIS JOURNAL*, **71**, 3049 (1949).

amount of benzoyl peroxide were mixed and the solution allowed to reflux for four hours as its temperature increased from 75 to 190°. The material was then distilled, and the 71 g. of distillate collected up to 190° at 50 mm. was fractionally redistilled in vacuum. Thirty-eight grams (42% yield) of low melting solid was obtained, b.p. 125–130° (15 mm.). The product appears to be largely a mixture of the monochlorides.

Anal. Calcd. for $C_8H_{12}ClBr$: mmoles of halogen per g. 8.95; for $C_8H_{11}Cl_2Br$: 11.63. Found: 9.17, 9.32.

Reaction of Monochloro-2-bromobicyclo[2,2,2]octane with Potassium *t*-Amyloxyde.—One hundred grams of *t*-amyl alcohol in which 11 g. (0.29 mole) of potassium had been dissolved and 22.2 g. (0.1 mole) of monochloro-2-bromobicyclo[2,2,2]octane was refluxed in a 200-ml. flask attached to a gas collection apparatus. After 40 hours about 400 ml. of gas, shown by its infrared spectrum to be ethylene, had been evolved. A titration at this time showed that 0.164 mole of base had been used up. The reaction mixture was shaken with water and the organic layer separated, dried and fractionally distilled. When the *t*-amyl alcohol had been removed the pot temperature rose above 170° without the distillation of any additional material.

Bicyclo[2,2,2]-2,5-octadiene.—Twenty grams (0.51 mole) of potassium and 250 ml. of aniline were placed in a three-necked flask equipped with a vapor-tight stirrer, thermometer, dropping funnel and Claisen distilling head leading through a condenser, receiver and drying tube to a gas collection apparatus. The system was swept with nitrogen and the aniline heated to reflux to dissolve the potassium. Then 38 g. (0.17 mole) of monochloro-2-bromobicyclo[2,2,2]octane in about 20 ml. of aniline was added slowly to the gently refluxing solution. Some material distilled during the addition of the chlorobromide, and when the addition was complete distillation was continued until the distillate temperature reached 170°. The distillate was washed with cold hydrochloric acid to remove the aniline and then dried over Drierite and fractionally distilled. At about 30° (155 mm.), 4 g. (30% yield) of benzene was collected and at 59–

61° (155 mm.), 1.5 g. (8% yield) of product was obtained. One liter of gas (24% yield), shown by its infrared spectrum to be ethylene containing a little acetylene, also was produced in the reaction.

The product of this and other similar preparations was found to have the properties: b.p. 126–127° (atm.), n_D^{25} 1.4912, d_4^{25} 0.9171.

Anal. Calcd. for C_8H_{10} : C, 90.50; H, 9.50. Found: C, 90.54; H, 9.54.

Reactions of Bicyclo[2,2,2]-2,5-octadiene (II).—Bromine was added to II until the red color was no longer discharged, and the resultant oil was cooled in Dry Ice until it crystallized. The crystals were washed with ethanol, recrystallized from ether–ethanol and then from hexane to yield white crystals, m.p. 103–103.5°.

Anal. Calcd. for $C_8H_{10}Br_4$: C, 22.56; H, 2.37; Br, 75.07. Found: C, 22.79, 22.75; H, 2.49, 2.52; Br, 74.71, 74.76.

When II was refluxed alone, in decalin or in aniline in which potassium had been dissolved for a time (30 minutes) longer than that which had been used in its synthesis, little, if any, gas was formed. However, when about 0.2 g. of II was refluxed under nitrogen so that the vapor came in contact with a wire coil heated to a dull red color, about 25 ml. of gas, shown by its infrared spectrum to be ethylene containing a little acetylene, was produced. The first few drops of distillate from the remaining liquid was shown, also by its infrared spectrum, to contain benzene.

Compound II was found to require 2.0 ± 0.2 moles of hydrogen for complete reduction. The white crystalline product had an infrared spectrum identical to the bicyclo[2,2,2]octane prepared by reduction of bicyclo[2,2,2]-2-octene.³⁰

Infrared Spectra.—The infrared spectra were determined using a Perkin–Elmer instrument, model 21. Samples were run in a 0.1-mm. cell and those run in solution were compensated with pure solvent in the same size cell.

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